

# PATENT ABSTRACTS OF JAPAN

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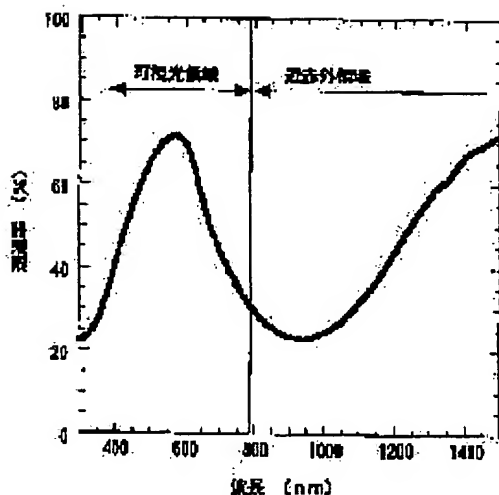
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(54) SUN RADIATION SCREENING MATERIAL, COATING SOLUTION FOR  
SUN RADIATION SCREENING MEMBRANE AND SUN RADIATION  
SCREENING MEMBRANE



(57)Abstract:

PROBLEM TO BE SOLVED: To prepare a coating solution that can form a membrane having high light transmission and low light reflection in the visible region, low transmission and high reflection in the near infrared region, electroconductivity controllable to about  $\geq 106 \Omega/\text{square}$  via a simple coating method in no need of expensive physical membrane formation method, and obtain a sun radiation- screening material to be used in the solution and a sun radiation-screening membrane prepared by using this material.

SOLUTION: This sun radiation-screening material contains particles of a hexaboride substance. This sun radiation-screening coating solution includes fine particles of hexaboride dispersed in a solution. In addition to the hexaboride particles, ATO, ITO, AZO may be used. In a preferred embodiment, the sun

radiation screening membrane has a surface resistance value of  $\geq 106 \Omega/\text{square}$ , further the permeability profile of the membrane has a maximum in the range of from 400 nm to 700 nm, while a minimum in the range of from 700 to 1,800 nm where the difference between the maximum and the minimum is  $\geq 5$  points.

[Claim(s)]

[Claim 1] The solar radiation shielding material containing 6 boride particle.

[Claim 2] The solar radiation shielding material whose X it is a solar radiation shielding material containing 6 boride (XB6) particle, and is one or more sorts in Ce, Gd, Tb, Dy, Ho, Y, Sm, Eu, Er, Tm, Yb, Lu, Sr, and calcium.

[Claim 3] Application liquid for solar radiation cover films which distributed 6 boride particle in the solution.

[Claim 4] Application liquid for solar radiation cover films with which particle size distributed 6 boride particle 200nm or less in the solution.

[Claim 5] Application liquid for solar radiation cover films according to claim 3 or 4 with which the partial hydrolysis polymerization object of the alkoxide of silicon, titanium, a zirconium, and aluminum or the alkoxide of aluminum is contained one or more sorts as a binder in application liquid.

[Claim 6] the claim 3 by which ultraviolet-rays hardening resin, a room-temperature-setting resin, or one or more sorts of thermoplastics is contained as a binder in application liquid - a claim 5 -- the application liquid for solar radiation cover films given in either

[Claim 7] The solar radiation shielding material which contains one or more sorts of an antimony content tin-oxide (ATO) particle, a tin content indium oxide particle (ITO), and an aluminum content zinc-oxide particle (AZO) further in addition to 6 boride particle.

[Claim 8] Application liquid for solar radiation cover films which distributed one or more

sorts of an antimony content tin-oxide (ATO) particle, a tin content indium oxide particle (ITO), and an aluminum content zinc-oxide particle (AZO) in the solution further in addition to 6 boride particle.

[Claim 9] The solar radiation cover film which applied the application liquid for solar radiation cover films according to claim 3 to 8 to the base material, and obtained it.

[Claim 10] The solar radiation shield which has the solar radiation cover film which applied the application liquid for solar radiation cover films according to claim 3 to 8 to the base material, and obtained it.

[Claim 11] The multilayer which makes a multilayer further this solar radiation cover film and one or more sorts of films with which refractive indexes differ in piles, and covers solar radiation efficiently using the interference effect of light on the solar radiation cover film which applied the application liquid for solar radiation cover films according to claim 3 to 8 to the base material.

[Claim 12] The multilayer according to claim 11 which used the best layer as the overcoat layer for protecting a film.

[Claim 13] The solar radiation cover film according to claim 9 whose surface-electrical-resistance values are more than 106ohms / \*\*.

[Claim 14] The multilayer according to claim 11 or 12 whose surface-electrical-resistance values are more than 106ohms / \*\*.

[Claim 15] The solar radiation cover film according to claim 9 whose difference of the maximal value and minimal value a membranous permeability profile has the maximal value in 400-700nm, and has the minimal value in 700-1800nm, and is 15 points or more.

[Claim 16] The multilayer according to claim 11 or 12 whose difference of the maximal value and minimal value a membranous permeability profile has the maximal value in 400-700nm, and has the minimal value in 700-1800nm, and is 15 points or more.

[Claim 17] The transparent base material which has the solar radiation cover function in which the solar radiation cover film or multilayer of one of the above was formed.

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[Translation done.]

## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the application liquid for applying to the base material which needs various solar radiation cover functions of glass, and plastics and others, such as an aperture of vehicles, a building, an office, and a common residence, a telephone booth, a show window, plastic film, and a lamp for lighting, and considering as a solar radiation cover film, the solar radiation shielding material used for this and the monolayer obtained by this, or a multilayer solar radiation cover film.

[0002]

[Description of the Prior Art] Considering as the method of removing and decreasing the heat component from sunlight etc., forming the thin film which reflects the wavelength of visible / infrared region in a glass front face, and considering as a heat reflective glass conventionally, was performed. As a material of a thin film used here, metallic oxides, such as FeOX, CoOX, CrOX, and TiOX, and the metallic material which has free electrons, such as Ag, Au, Cu, nickel, and aluminum, so much were chosen.

[0003] However, such material had the property which also reflects or absorbs the light of a light field simultaneously in addition to the near infrared ray which contributes to a thermal effect greatly especially by sunrays, and had the fault to which a visible light transmittance falls.

[0004] Therefore, the operation which the high permeability of a light field is needed when using such material for the transparent base material in building materials, a vehicle, a telephone booth, etc., and makes thickness very thin was required. And it has been formed membranes and used for the very thin thin film of 10nm level using the physical forming-membranes methods, such as spray baking, CVD, or a spatter, a vacuum deposition method. These membrane formation methods needed large-scale equipment and the vacuum facility, and the problem was in productivity and large area-ization, and they were still higher. [ of the membranous manufacturing cost ]

[0005] Moreover, with such material, when it was going to make the visible light transmittance high, the solar radiation cover property fell, and the property in which the building envelope which the visible light transmittance fell and gave the film would become dark if a solar radiation cover property is conversely made high was held.

[0006] Moreover, with such material, the reflection factor of a light field also tended to become high simultaneously, and had the fault which gives appearance [ GIRAGIRA / appearance ] like a mirror and spoils a fine sight.

[0007] Furthermore, with such material, there were many to which membranous conductivity becomes high, the cellular phone and the electric wave of TV reception were reflected in this case, it became non-receipt and there was a fault, such as causing an electromagnetic interference in a circumference area.

[0008] In order to improve the above faults, as a membranous physical property, the permeability of the light of a light field was high, the permeability of the light of a near infrared region was low, the reflection factor of the light of a light field was low, and the reflection factor of the light of a near infrared region was high, and membranous conductivity needed to form the film about controllable 106ohms / more than \*\*.

[0009] However, the material which forms such [ conventionally ] a film or such a film was not known.

[0010] A visible light transmittance is high and the antimony content tin oxide (ATO), and tin content indium oxide (ITO) and an aluminum content zinc oxide (AZO) are known by material with a heat ray cover function. Such material had the comparatively low rate of a visible light reflex, although the appearance [ GIRAGIRA / appearance ] was not given, plasma wave length was in the long wavelength side comparatively, and reflection and the absorption effect of these films in the near-infrared region near the light were not enough. Moreover, when these films were formed by the physical forming-membranes method, membranous conductivity went up and there was a fault which causes reflective disturbance of the above-mentioned electric wave.

[0011]

[Problem(s) to be Solved by the Invention] Then, this invention solves the trouble of the above-mentioned conventional technology, and its reflection factor is [ the permeability of the light of a light field is high and ] low. The application liquid for forming membranes by the simple applying method, without the permeability of the light of a near infrared region being low, and a reflection factor being high, and membranous conductivity using the physical forming-membranes method of high cost for a film about controllable 106ohms / more than \*\*, It aims at offering the solar radiation shielding material used for this, and the solar radiation cover film using this.

[0012]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention persons by ultrafine-particle-izing this and producing the film distributed highly variously as a property of the material itself paying attention to 6 borides which hold a free electron so much as a result of examination The phenomenon of both discovering absorption and reflection strong against the near-infrared region near a light field for the maximum of permeability to a light field, and coming to have the minimum of permeability in it is found out. Furthermore, it found out that these properties were notably seen to 6 borides, and could form membranous surface electrical resistance by the easy applying method, without using the physical forming-membranes method of high cost for a film controllable 106ohms / more than \*\*, and resulted in this invention.

[0013] That is, the solar radiation shielding material of this invention is characterized by containing 6 boride particle. When 6 borides are written by "XB6" here, it is desirable for X to be one or more sorts in Ce, Gd, Tb, Dy, Ho, Y, Sm, Eu, Er, Tm, Yb, Lu, Sr, and calcium.

[0014] The application liquid for solar radiation cover films of this invention is characterized by distributing 6 boride particle in a solution, and 6 boride particle 200nm or less is desirably distributed for particle size in a solution. in application liquid desirably moreover, as a binder the alkoxide of silicon, titanium, a zirconium, and aluminum -- or It is good to contain the partial hydrolysis polymerization object of the alkoxide of aluminum one or more sorts, and to contain ultraviolet-rays hardening resin, a room-temperature-setting resin, or one or more sorts of thermoplastics as a binder in application liquid desirably.

[0015] In addition to 6 boride particle, one or more sorts of an antimony content tin-oxide (ATO) particle, a tin content indium oxide particle (ITO), and an aluminum content zinc-oxide particle (AZO) may contain further other solar radiation shielding materials of this

invention.

[0016] The solar-radiation cover film of this invention is good also as a multilayer which applies the application liquid for solar-radiation cover films of one of the above to a base material, obtains it, makes a multilayer further this solar-radiation cover film and one or more sorts of films with which refractive indexes differ in piles, and covers solar radiation efficiently using the interference effect of light, and good also as an overcoat layer for protecting a film for the best layer in this case.

[0017] It is good in the solar radiation cover film of this invention being desirable, surface-electrical-resistance values being more than 106ohms / \*\*, and a membranous permeability profile having the maximal value in 400-700nm, and they having the minimal value in 700-1800nm desirably, and the difference of the maximal value and minimal value being 15 points or more.

[0018] Moreover, the transparent base-material transparent base material which has the solar radiation cover function of this invention is a transparent base material which has the solar radiation cover film or multilayer of one of the above.

[0019]

[Embodiments of the Invention] Although 6 boride particle whose X is Ce, Gd, Tb, Dy, Ho, Y, Sm, Eu, Er, Tm, Yb, Lu, Sr, and calcium is mentioned as the typical thing when 6 boride particle used for this invention is written by "XB6", even if it is these two or more sorts of mixture, and 6 borides other than these, a solar radiation shielding effect is obtained.

[0020] Although it is desirable that the front face has not oxidized as for 6 boride particle, it is not avoided to some extent that have usually oxidized in many cases slightly, and surface oxidization takes place at the distributed process of a particle. However, there is no change in the effectiveness which discovers a solar radiation shielding effect also by that case.

[0021] Moreover, these 6 boride particles will discover a solar radiation shielding effect, if the fundamental combination inside a particle has the structure of cubic CaB6 type even if it seems that crystallinity produces a diffraction peak [ low and very broadcloth in an X diffraction ].

[0022] Although these 6 boride particles are the powder colored dark purple-blue etc., particle size is small enough compared with visible light wave length, and visible light-transmission nature arises on a film in the state where it distributed in the thin film. However, infrared light cover ability can be held sufficiently strongly. Although this reason is not understood in detail, these material holds comparatively many free electrons, and it is thought that absorption by the interband transition between 4f-5d, the electronic-electron, and the electron phonon interaction originates in existing in a near infrared region.

[0023] According to the experiment, by the film which distributed these particles sufficiently finely and uniformly, having the maximal value, while permeability is the wavelength of 400-700nm, and having the minimal value with a wavelength of 700-1800nm in between is observed. If visible light wave length takes into consideration that it is 380-780nm and visibility is campanulate [ with a peak of near 550nm ], by such film, he penetrates the light effectively and can understand absorbing and reflecting the other solar radiation effectively.

[0024] The ITO particle used by the case, an ATO particle, and an AZO particle have

large reflection and absorption which there is almost no absorption of light in a light field, and originates in a plasmon in a field 1000nm or more. Therefore, it becomes possible to cover efficiently the reradiation of the heat energy absorbed by the sunrays of a near infrared region, and surface of the earth, without decreasing a visible light transmittance so much by using it together with the above-mentioned 6 boride particle, and the effect of raising a heat ray cover property is acquired.

[0025] The particle size of 6 boride particle in application liquid has good 200nm or less, and its 100nm or less is preferably good. It is because it will become difficult to reduce solar radiation permeability efficiently, a mountain of a profile and a difference of a valley which have the maximal value and have the minimal value with a wavelength of 700-1800nm in between becoming small, and maintaining a visible light transmittance enough, while a characteristic permeability profile which was described above, i.e., permeability, was the wavelength of 400-700nm if a particle diameter becomes larger than 200nm. Moreover, it is because the condensation inclination of the particles in dispersion liquid becomes strong and causes [ of a particle ] sedimentation, when a particle diameter is larger than 200nm.

[0026] Since the particles exceeding 200 nm or those big and rough particles that were condensed become the cause by which become a source of light scattering, and produce cloudiness (Hayes) on a film or a visible light transmittance decreases on it, they are not desirable. in addition, the minimum particle size available on an economic target is about 2nm with the present technology

[0027] The particle size of the ITO particle used by the case, an ATO particle, or an AZO particle also has good 200nm or less, and its 100nm or less is preferably good. It is because the condensation inclination of the particles in dispersion liquid will become strong and will cause [ of a particle ] sedimentation, if a particle diameter becomes larger than 200nm. Moreover, like the above, since the particles exceeding 200nm or those big and rough particles that were condensed become the cause by which become a source of light scattering, and produce cloudiness (Hayes) on a film or a visible light transmittance decreases on it, they are not desirable. in addition, the minimum particle size available on an economic target is about 2nm with the present technology

[0028] Especially the dispersion medium of the particle in application liquid is not limited, and is selectable according to the alkoxide in application conditions, application environment, and application liquid, a synthetic-resin binder, etc., for example, its various kinds of organic solvents, such as water, alcohol, the ether, ester, and a ketone, are usable. Moreover, an acid and alkali may be added if needed and pH may be adjusted. Furthermore, in order to raise the distributed stability of the particle in application liquid further, it is also possible to add various kinds of surfactants, a coupling agent, etc. Each addition at that time is 5 or less % of the weight preferably 30 or less % of the weight to a non-subtlety particle.

[0029] Since conductivity of the film using this application liquid is performed along with the electric conduction path which went via the contact part of a particle, it can cut an electric conduction path partially by adjusting the amount of a surfactant or a coupling agent, and can reduce membranous conductivity easily to the surface-electrical-resistance value 106ohms / more than \*\*. Moreover, conductive control is possible also by adjusting the content of silicon, a zirconium, titanium, the alkoxides of each metal of aluminum, these partial hydrolysis polymerization objects, or a synthetic-resin binder.

[0030] The distributed method of the above-mentioned particle can be arbitrarily chosen, if it is the method which a particle distributes in a solution uniformly. As an example, methods, such as a bead mill, a ball mill, a sand mill, and ultrasonic distribution, can be mentioned.

[0031] On a base material, the above-mentioned particle deposits the solar radiation cover film of this invention with high density, and it forms a film. If silicon, a zirconium, titanium, the alkoxide of each metal of aluminum, the partial hydrolysis polymerization object of these metals, or a synthetic-resin binder is included in application liquid, the binding property to the base material of a particle will improve application liquid after an application and hardening, and a membranous degree of hardness will improve further. Moreover, the binding capacity to the base material of the film which makes a particle a principal component, a membranous degree of hardness, and weatherability can be further raised by forming in piles the layer which contains the adding-water part depolymerization object or synthetic resin of each metal alkoxide, such as silicon, a zirconium, titanium, and aluminum, or these metal alkoxide further on the film obtained by doing in this way.

[0032] When it does not include silicon, a zirconium, titanium, the alkoxide of each metal of aluminum, the adding-water part depolymerization object of these metals, or a synthetic-resin binder in application liquid, the film obtained after applying this application liquid to a base material becomes the membrane structure which only the above-mentioned particle deposited on the base material. Although a solar radiation shielding effect is shown also with this On this film, further like the above Silicon, a zirconium, titanium, the alkoxide of each metal of aluminum, Or since an application liquid component fills the gap which the particle of the 1st layer deposited and is formed by applying the application liquid containing the adding-water part depolymerization object or synthetic-resin binder of these metals, forming a coat, and considering as a multilayer, Membranous Hayes decreases, and a visible light transmittance improves, and the binding property to the base material of a particle improves.

[0033] As a method of binding the film which makes the above-mentioned particle a principal component with the coat which consists of silicon, a zirconium, titanium, an alkoxide of each metal of aluminum, or a adding-water part depolymerization object of these metals, although a spatter and a vacuum deposition are also possible, an advantage, like the easy pod cost of a membrane formation process is low to the applying method is effective. This application liquid for coats has 40 or less desirable % of the weight in [ all ] a solution at the oxide conversion from which two or more sorts are included and the content liquid is obtained [ one sort or ] after heating in water or alcohol in silicon, a zirconium, titanium, the alkoxide of each metal of aluminum, or the adding-water part depolymerization object of these metals. Moreover, it is also possible to add an acid and alkali if needed and to adjust pH.

[0034] By applying such liquid as the 2nd layer further on the film which makes the above-mentioned particle a principal component, and heating it, oxide coats, such as silicon, a zirconium, titanium, and aluminum, are easily producible. Moreover, it applies as the 2nd layer further on the film which makes the above-mentioned particle a principal component, and can be made to be able to harden using the thermoplastics currently generally used in addition to these alkoxides, and a room-temperature-setting resin and ultraviolet-rays hardening resin, and a resin coat can also be produced easily.



[0035] Moreover, it is possible by applying a film with the refractive index of a particle distribution film, and a different refractive index to a multilayer in piles to raise further the solar radiation cover property made into the purpose using the interference effect of the light by the refractive-index difference in the interface of each film.

[0036] Especially as the method of application of application liquid and the application liquid for coats, it is not limited, and if the spin coat method, a spray coating method, a dip coating method, screen printing, the roll coat method, flow coating, etc. are flatness and the method of applying uniformly thinly, they can adopt processing liquid suitably by any methods.

[0037] The base-material heating temperature after the application of the application liquid containing each above-mentioned metal alkoxide and its adding-water part depolymerization object Since the polymerization reaction of the alkoxide contained in a paint film at less than 100 degrees C and its adding-water part depolymerization object remains in many cases by un-completing, and water and an organic solvent remain in a film and it becomes the cause of reduction of the visible light transmittance of the film after heating To heat desirable still more preferably above the boiling point of the solvent in application liquid has good 100 degrees C or more.

[0038] Moreover, what is necessary is just to irradiate ultraviolet rays suitably that what is necessary is just to make it harden according to the respectively optimal hardening method, if it is ultraviolet-rays hardening resin, when a synthetic-resin binder is used. Moreover, in order for what is necessary to be just to leave it as it is after the application if it is a room-temperature-setting resin, an application in the site to the existing windowpane etc. is possible, and versatility spreads.

[0039] As a binder component used for the application liquid of this invention, you may use the ORGANO silazane solution as application liquid for overcoats. As an ORGANO SHIZARAN solution, the thing 100 degrees C or less is also marketed for the polymerization curing temperature by correction of a side chain radical, or addition of an oxidation catalyst, and membrane formation temperature can be made quite low by using these.

[0040] Since it is the film which the above-mentioned particle distributed by the film of this invention, there is little reflection in a light field compared with a film with the mirror-plane-like front face where the crystal filled the inside of a film precisely like the oxide thin film manufactured by the physical forming-membranes method, and it can avoid presenting the appearance [ GIRAGIRA / appearance ]. Moreover, the multilayer of 1% or less of luminous reflectances can be easily manufactured by forming a film of a low refractive index like SiO<sub>2</sub> or MgF on this particle distribution film to suppress reflection of a light field further.

[0041] In application liquid, it is also still more possible to mix particles, such as ATO, ITO, and AZO. Since absorption in the near-infrared-ray field near the light will increase if an addition is increased, these transparent particles can be considered as the high solar radiation cover film of a visible light transmittance. Moreover, it is also possible to assist the heat ray shielding effect at the same time it adds the application liquid of this invention conversely in the liquid which carried out particle distribution, such as ATO, ITO, and AZO, and colors a film. In this case, a solar radiation shielding effect can be assisted with few additions of \*\* to ITO used as a subject etc.

[0042] The application liquid by this invention distributes a non-subtlety particle, and

since it is not what forms the target heat ray cover film using the decomposition or the chemical reaction of an application component by the heat at the time of baking, it can form the transparency film of the uniform thickness by which the property was stabilized.

[0043] A particle deposits the particle distribution film in this invention with high density, it forms a film on a base material, and the alkoxides, these adding-water part depolymerization objects, or the synthetic-resin binder of each metal of the silicon contained in application liquid, a zirconium, titanium, and aluminum is effective in raising the binding property to the base-material top of a particle after hardening of a paint film, and raising membranous intensity further.

[0044] Thus, although manufacture of the film which has a heat ray shielding effect by mixing the material of the above-mentioned inorganic particle suitably is possible according to this invention, since such particle material is inorganic material, even if weatherability is very high compared with an organic material, for example, it uses it for the part which sunrays (ultraviolet rays) hit, degradation of a color or many functions is hardly produced.

[0045]

[Example] Hereafter, an example explains this invention to a detail more.

Example 1 ... 20g [ of CeB6 particles ] (90nm of mean particle diameters) and diacetone alcohol (DAA) 78g and 2.0g of coupling agents for particle distribution were mixed, ball mill mixture was carried out for 150 hours using the zirconia ball with a diameter of 4mm, and 100g of dispersion liquid of CeB6 particle was produced (A liquid).

[0046] Next, ethanol 30g was well mixed in 70g of ethyl-silicate solutions which adjusted the ethyl silicate 40 (the Tama chemical-industry incorporated company make) which are 4 - a pentamer with average degree of polymerization by 25g, ethanol 32g, 8g of 5% hydrochloric-acid solution, and 5g of water, 100g of ethyl-silicate mixed liquor was adjusted to them, and this was used for them as a binder (B liquid).

[0047] A liquid and B liquid were diluted with ethanol, and were enough mixed so that it might become composition of Table 1, and rotation was stopped, after dropping 15g of this solution from the beaker on the 200x200x2mm soda lime system board glass substrate rotated by 150rpm and shaking it off for 5 minutes as it was. This was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained.

[0048] Using the Hitachi spectrophotometer, the permeability of the formed film measures the permeability of 200-1800nm, and is JIS. R According to 3106, solar radiation permeability ( $\tau_{\text{ue}}$ ) and the visible light transmittance ( $\tau_{\text{uv}}$ ) were computed. These results are shown in Table 1. The property of the film obtained in examples 2-16 and the example 1 of comparison was also collectively shown in Table 1. Moreover, the typical profile of this film is shown in drawing 1 :

[0049] Example 2 ... Except having made CeB6 particle of A liquid of an example 1 into GdB6 particle (85nm of mean particle diameters), application liquid adjustment and the spin coat were carried out by the same method as an example 1, and this was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0050] Example 3 ... Application liquid is adjusted by the same method as an example 1 except having made CeB6 particle of A liquid of an example 1 into TbB6 particle (90nm of mean particle diameters). This was diluted with ethanol until particle concentration

became 2.0% of the weight, and rotation was stopped, after dropping 15g of this solution from the beaker on the 200x200x3mm soda lime system board glass substrate rotated by 200rpm and shaking it off for 5 minutes as it was. Rotation was stopped, after dropping from the beaker 15g of solutions which diluted SiO<sub>2</sub> concentration of B liquid with ethanol to 2.0% further on the above-mentioned application substrate rotated by 150rpm and shaking them off for 5 minutes as it was besides. This was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0051] Example 4 ... Except having made CeB6 particle of A liquid of an example 1 into DyB6 particle (95nm of mean particle diameters), application liquid adjustment and the spin coat were carried out by the same method as an example 1, and this was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0052] Example 5 ... Except having made CeB6 particle of A liquid of an example 1 into HoB6 particle (85nm of mean particle diameters), application liquid adjustment and the spin coat were carried out by the same method as an example 1, and this was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0053] Example 6 ... Except having made CeB6 particle of A liquid of an example 1 into YB6 particle (90nm of mean particle diameters), application liquid adjustment and the spin coat were carried out by the same method as an example 1, and this was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0054] Example 7 ... CeB6 particle of A liquid of an example 1 is made into YB6 particle (90nm of mean particle diameters). Instead of B liquid, application liquid adjustment and a spin coat are carried out by the same method as an example 1 except having used the silicone system UV hardening resin by the Shin-etsu silicone company as a binder. After having put this into the 100-degree C electric furnace, drying for 2 minutes and evaporating a solvent, UV irradiation was carried out for 2 minutes using the high pressure mercury vapor lamp, and the target film was obtained. The optical property of this film is shown in Table 1.

[0055] Example 8 ... Instead of B liquid, CeB6 particle of A liquid of an example 1 was made into EuB6 particle (90nm of mean particle diameters), the urethane lacquer by Mitsui Chemicals, Inc. was used as a binder, except having set the spin rotational frequency to 200rpm, application liquid adjustment and the spin coat were carried out by the same method as an example 1, this was left at the room temperature, the solvent was evaporated, and the target film was obtained. The optical property of this film is shown in Table 1.

[0056] example 9 ... instead of B liquid, CeB6 particle of A liquid of an example 1 was made into ErB6 particle (120nm of mean particle diameters), the room-temperature-setting resin by the Shin-etsu silicone company was used as a binder, except having set the spin rotational frequency to 200rpm, application liquid adjustment and the spin coat were carried out by the same method as an example 1, this was left at the room temperature, the solvent was evaporated, and the target film was obtained. The optical property of this film is shown in Table 1.

[0057] Example 10 ... Except having made CeB6 particle of A liquid of an example 1

into TmB6 particle (110nm of mean particle diameters), application liquid adjustment and the spin coat were carried out by the same method as an example 1, and this was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0058] Example 11 ... Except having made CeB6 particle of A liquid of an example 1 into LuB6 particle (95nm of mean particle diameters), application liquid adjustment and the spin coat were carried out by the same method as an example 1, this was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0059] Example 12 ... Except having made CeB6 particle of A liquid of an example 1 into SrB6 particle (95nm of mean particle diameters), application liquid adjustment and the spin coat were carried out by the same method as an example 1, this was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0060] Example 13 ... Except having made CeB6 particle of A liquid of an example 1 into CaB6 particle (80nm of mean particle diameters), application liquid adjustment and the spin coat were carried out by the same method as an example 1, this was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0061] Example 14 ... Except having made CeB6 particle of A liquid of an example 1 into TbB6 particle (80nm of mean particle diameters), application liquid adjustment and the spin coat were carried out by the same method as an example 1, this was put into the 180-degree C electric furnace, it heated for 30 minutes, and the target film was obtained. The optical property of this film is shown in Table 1.

[0062] Example 15 ... 35g [ of ITO particles ] (55nm of mean particle diameters) and diacetone alcohol (DAA) 61g and 4.0g of coupling agents for particle distribution were mixed, ball mill mixture was carried out for 12 hours using the zirconia ball with a diameter of 4mm, and 100g of dispersion liquid of an ITO particle was produced (C liquid). This C liquid, A liquid of an example 1, and the silicone system UV hardening resin by the Shin-etsu silicone company were diluted with ethanol so that it might become composition of the example 20 of Table 1, it was mixed enough, and rotation was stopped, after dropping 15g of this solution from the beaker on the 200x200x3mm soda lime system board glass substrate rotated by 200rpm and shaking it off for 5 minutes as it was. After having put this into the 100-degree C electric furnace, drying for 2 minutes and evaporating a solvent, UV irradiation was carried out for 2 minutes using the high pressure mercury vapor lamp, and the target film was obtained. The optical property of this film is shown in Table 1.

[0063] Example 16 ... 35g [ of ATO particles ] (50nm of mean particle diameters) and diacetone alcohol (DAA) 61g and 4.0g of coupling agents for particle distribution were mixed, ball mill mixture was carried out for 12 hours using the zirconia ball with a diameter of 4mm, and 100g of dispersion liquid of an ITO particle was produced (D liquid). This D liquid, A liquid of an example 1, and the silicone system UV hardening resin by the Shin-etsu silicone company were diluted with ethanol so that it might become composition of the example 20 of Table 1, it was mixed enough, and rotation was stopped, after dropping 15g of this solution from the beaker on the 200x200x3mm soda lime system board glass substrate rotated by 200rpm and shaking it off for 5 minutes

as it was. After having put this into the 100-degree C electric furnace, drying for 2 minutes and evaporating a solvent, UV irradiation was carried out for 2 minutes using the high pressure mercury vapor lamp, and the target film was obtained. The optical property of this film is shown in Table 1.

[0064] In the above examples 1-16, while solar radiation permeability is 15 points or more low by percentage and maintains a luminosity rather than a visible light transmittance about all films, it turns out well that solar radiation is covered efficiently, and it turns out that it is useful as a solar radiation cover film. Moreover, it was confirmed that the reflection factor in a light field is 8% or less, and not all the films of an example have a mirror-like flash, and surface-electrical-resistance values are more than  $8 \times 10^{10} \text{ohms} / **$  by all films further, and it is satisfactory in electric wave permeability.

[0065] Example 1 of comparison ... About the heat reflective glass of marketing produced by the physical forming-membranes method of high cost compared with the applying method, 340-1800nm spectral transmittance is measured, and it is JIS. R When the optical property was investigated according to 3106, it became 61.8% of visible light transmittances, and 63.4% of solar radiation permeability. This has the small difference of a visible light transmittance and solar radiation permeability as compared with the above-mentioned 6 boride application film, and a solar radiation shielding efficiency is bad. Moreover, the rate of a visible light reflex was very as high as or more 30%, and was presenting the appearance of the shape of a mirror [ GIRAGIRA / appearance / shape ]. The surface-electrical-resistance value of a film surface was as low as  $83 \text{ohms} / **$ , and it was clear to electric wave permeability and reflection nature that there is a problem again.

[0066]

[Table 1]

		塗布液中の 固 形 分 量 (重量%)			光 学 特 性		
	含有微粒子の 種 類	微 粒 子	バイン ダー		τ <sub>V</sub> (%)	τ <sub>R</sub> (%)	透過率の 極大値と極 小値の差
実施例1	CeB6	1.5	1.5	無し	68.5	44.3	48.5
実施例2	GdB6	1.5	1.5	無し	68.1	52.8	32.3
実施例3	TbB6	2.0	0.0	有り	54.0	38.4	31.2
実施例4	DyB6	1.5	2.0	無し	65.8	50.2	33.0
実施例5	HoB6	2.0	2.0	無し	48.7	33.0	28.4
実施例6	YB6	1.2	1.5	無し	76.3	53.1	47.6
実施例7	SmB6	1.8	10.0	無し	66.5	39.1	33.7
実施例8	EuB6	1.8	15.0	無し	54.2	38.3	30.5
実施例9	ErB6	2.0	20.0	無し	50.9	34.0	33.3
実施例10	TmB6	2.0	0.8	無し	46.0	30.9	30.2
実施例11	LuB6	1.5	0.8	無し	64.3	43.1	35.2
実施例12	SrB6	1.0	1.5	無し	77.2	61.3	25.6
実施例13	CaB6	1.0	1.5	無し	78.2	61.9	24.3
実施例14	YbB6	1.5	1.5	無し	83.8	48.4	31.2
実施例15	CeB6/ITO	0.8/20	20.0	無し	70.5	37.3	—
実施例16	CeB6/ATO	0.8/20	20.0	無し	67.3	40.2	—
比較例1	日射遮蔽ガラス	—	—	—	61.8	63.4	—

[0067]

[Effect of the Invention] As shown above, according to this invention, the permeability of the light of a light field is high. the permeability of the light of a near infrared region to a low sake Can cover the heat energy of solar radiation efficiently, without spoiling a luminosity, and the rate of a visible light reflex does not have a flash at a low's. Since membranous conductivity can control 106ohms / more than \*\*, it is the solar radiation cover film excellent in electric wave permeability, and the application liquid which can form this by the simple applying method, without using the physical forming-membranes method of high cost, and the solar radiation cover film using this have been offered.

[0068] It is effective in reducing the cooling load of summer by using this film for windowpanes, such as a building, is useful also to energy saving, and is an industrial product with usefulness high also in environment.

[Translation done.]

## DRAWINGS

[Drawing 1]

